Facile synthesis of dicyanovinyl-di(*meso*-aryl)dipyrromethenes *via* a dipyrromethene–DDQ adduct†

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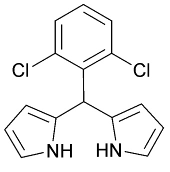
Received 4th March 2009, Accepted 6th April 2009
First published as an Advance Article on the web 15th April 2009
DOI: 10.1039/b904446a

The dicyano-substituted vinyl dipyrromethene 4 and compound 5 are near-planar and were prepared from a simple *meso*-aryl dipyrromethane *via* the DDQ adduct 3; the unique structures of 3, 4 and 5 were confirmed by X-ray diffraction analysis.

2,3-Dichloro-5,6-dicyano-1,4-quinone (DDQ) has been used as a powerful oxidant during the synthesis of polyaryl compounds, and these oxidation processes have been intensively studied over the past few decades.[1] Initial radical formation to give resonance-stabilized intermediates is considered to be the principal oxidation mechanism.[2] In addition, 1,4-benzoquinones bearing electron-withdrawing groups are strong dienophiles. Several DDQ adducts have been prepared as precursors toward the aromatization of saturated compounds.[3] Such aromatization is achieved by DDQ elimination *via* thermal processes in the presence of a DDQ acceptor. Recently, we reported the isolation of a C_2-symmetric hexapyrrole by the oxidation of *meso*-2,6-dichlorophenyl tripyrrane using DDQ under aerobic conditions.[4] Here, a unique DDQ adduct, compound **3**, in which the DDQ moiety has linked two dipyrromethene units, has been isolated from the simple DDQ oxidation of *meso*-2,6-dichlorophenyl-dipyrromethane (**1**).‡ In addition to acting as a simple oxidant, the current work shows that DDQ can form adducts with specific substrates, which can the undergo subsequent transformations. Other dipyrromethanes having different *meso*-substituents, such as 4-nitrophenyl, 4-chlorophenyl and perfluorophenyl groups, were also treated with DDQ under the same reaction conditions. Only the perfluorophenyl-substituted dipyrromethane formed a DDQ adduct in a reasonable yield (~20%) (see ESI†). The strong electron-withdrawing groups seem to play a key role in this reaction. Thus, treatment of adduct **3** with Et_3N gave a new compound **4** resulting from the partial elimination of the DDQ moiety. Alternatively, refluxing a THF solution of **3** in the presence of $AlCl_3$ and MeOH formed **5**. The structures of **3**, **4** and **5** have been confirmed by X-ray diffraction analysis.§

These two products, **2** and **3**, were prepared by the overnight DDQ oxidation reaction of *meso*-2,6-dichlorophenyl-dipyrromethane (**1**) in CH_2Cl_2 and isolated using column chromatography on silica gel with CH_2Cl_2–hexane (3:2) as eluent.‡



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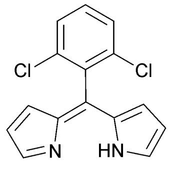

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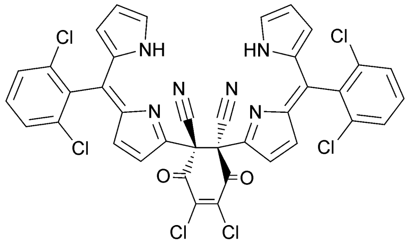

3

The first, least polar, fraction (**3**) is red in organic solvents, and single crystals were obtained by the addition of hexane vapor into a $CHCl_3$ solution. The second (yellow) fraction was the dipyrromethene **2**. When pure compound **2** was treated with excess DDQ, **3** was not obtained. Only dipyrromethane **1** produced **3** during the oxidation step. As shown in Fig. 1, the structure of **3** showed DDQ to be joined at the *A*-positions of the dipyrromethenes, with a *trans*-configuration around the C–C bond of the two sp^3 carbon atoms of the original DDQ. The amino-nitrogens share a hydrogen atom with the imino-nitrogen and the oxo-oxygen by hydrogen-bonding to create near-C_2 symmetry. Consequently, the DDQ ring is slightly tilted in order to make the oxygen atoms point towards the amino-NH. Furthermore, the mean planes of the two dipyrromethenes are nearly coplanar and perpendicular to

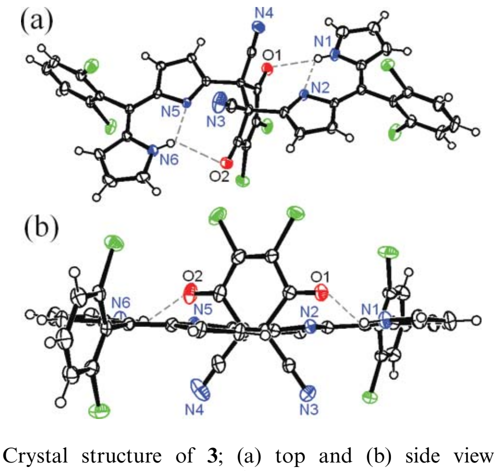

Fig. 1 Crystal structure of **3**; (a) top and (b) side views; hydrogen-bond (dashed lines) lengths (Å): 2.25(3) [N(1)–H···N(2)], 2.55(3) [N(1)–H···O(1)], 2.19(3) [N(6)–H···N(5)], 2.50(3) [N(6)–H···O(2)].

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† Electronic supplementary information (ESI) available: Experimental and spectral data for compounds, crystallographic data for compounds **3**, **4** and **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904446a

the DDQ-plane. The symmetry of **3** in solution was confirmed in the ^{1}H NMR spectrum, where only four β-protons were observed (Fig. 3a). A broad NH peak was observed downfield at 11.18 ppm due to the hydrogen-bonding. In addition, the sp^3 nature of the cyanide-bearing carbon atoms was confirmed at 30.28 ppm in the ^{13}C NMR spectrum (see ESI†). The optical spectrum of **3** (Fig. 4) showed a bathochromic shift (69 nm) for the two dipyrromethene units compared to that of the dipyrromethene (**2**).

When compound **3** was treated with Et_3N (Scheme 1), the red color dramatically changed to green. X-Ray crystallographic analysis revealed the structure **4**, as shown in Fig. 2, in which DDQ was partially eliminated and a double bond was newly formed with concomitant extension of the π-conjugated network along the main skeleton. The mean plane of the main skeleton exhibited near-planarity (see the side-view in Fig. 2b). Due to the extended π-conjugation, the sets of neighboring β-hydrogen peaks were widely separated in the ^{1}H NMR spectrum (the red and blue lines denote the peaks of β-hydrogens on the inner and outer pyrroles in Fig. 3). The cyano-nitrogens also act as hydrogen-bond acceptors and result in the NH peaks being extremely broadened and highly downfield-shifted (12.94 ppm) in comparison to those of compound **3** (Fig. 3b). The downfield shift of one of the pyrrole β-hydrogens also results from intra-molecular hydrogen bonding with the cyano-nitrogen. The extended π-conjugation also generated a lower energy absorption band in its optical spectrum (Fig. 4).

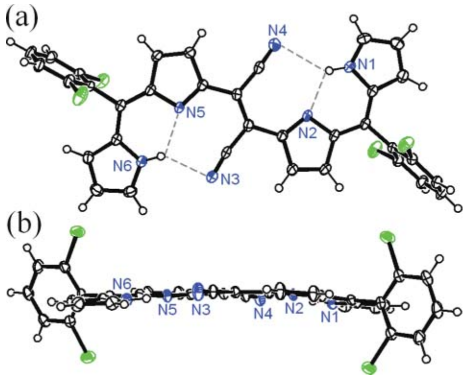
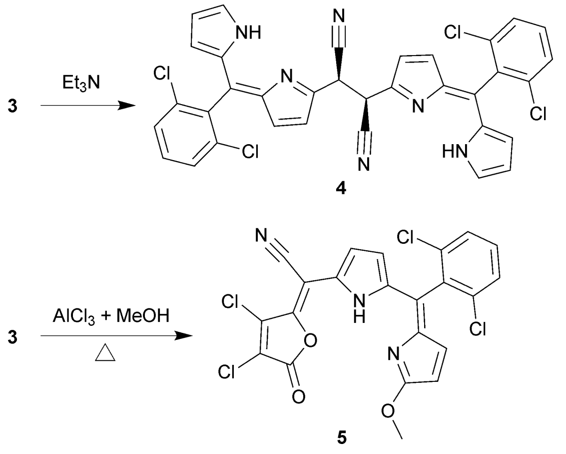


Fig. 2 Crystal structure of **4**; (a) top and (b) side views. The hydrogen-bond (dashed lines) lengths (Å): 2.16(2) [N(1)–H···N(2)], 2.31(2) [N(1)–H···N(4)], 2.52(2) [N(5)–H···N(3)], 2.13(2) [N(5)–H···N(6)].



Scheme 1 Formation of **4** and **5** from **3**.

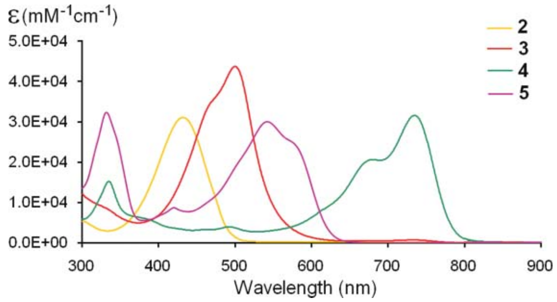


Fig. 4 Optical spectra of **2**–**5** in CH_2Cl_2.

The elimination to give **4** from **3** has aspects of a reverse Diels–Alder reaction, and it is possible that, after attack of the nucleophile, a concerted elimination does indeed occur to give a "diketene". However, considering the considerable resonance stabilization of the carbanion, it is equally likely that the elimination proceeds through this intermediate.

A dipyrromethene-eliminated compound **5** was obtained by refluxing a THF solution of **3** in the presence of $AlCl_3$ and MeOH followed by purification using column chromatography. A single crystal of **5** was grown by diffusion of hexane into a CH_2Cl_2 solution. The structure (Fig. 5) exhibits an oxo-furan ring, and Scheme 2 describes a mechanism for its formation. The oxo-oxygen and imino-nitrogen atoms act as hydrogen-bond acceptors

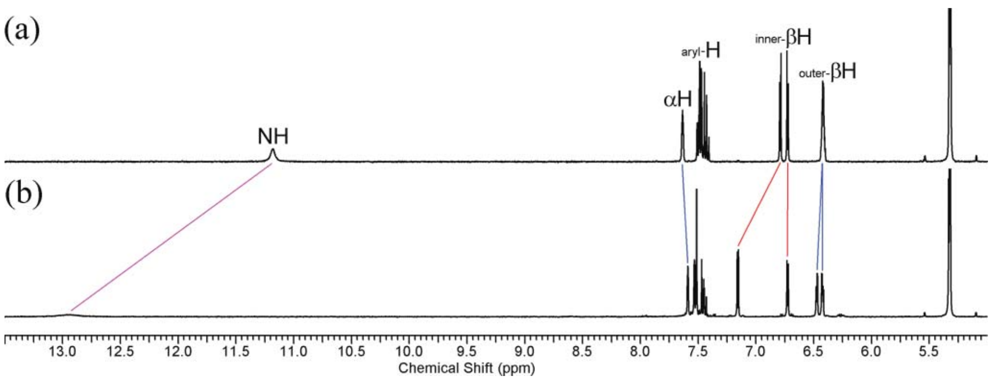
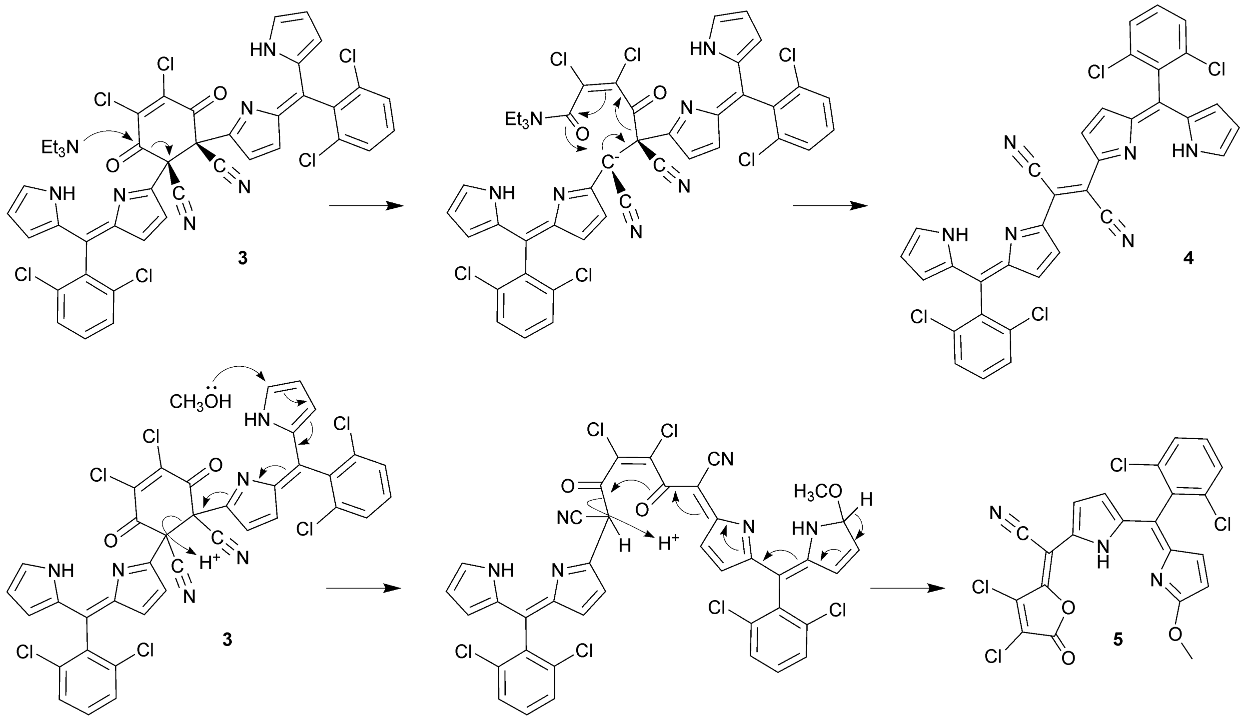


Fig. 3 ^{1}H NMR spectra of (a) **3** and (b) **4** in CD_2Cl_2.



Scheme 2 A possible mechanism for the formation of **4** and **5** from **3**.

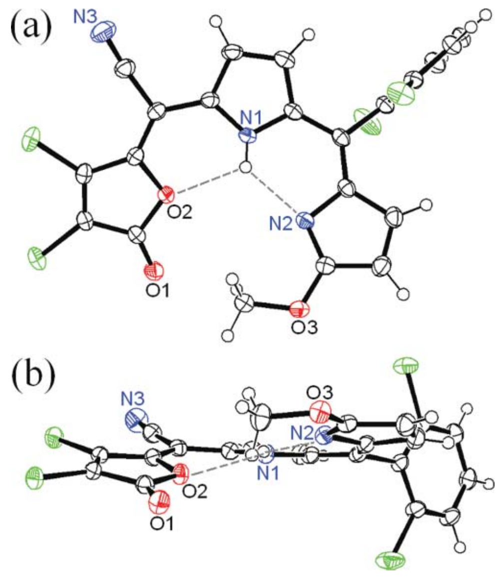


Fig. 5 Crystal structure of **5**; (a) top and (b) side views; hydrogen-bond (dashed lines) lengths (Å); 2.360(19) [N(2)–H···O(1)], 2.140(17) [N(2)–H···N(1)].

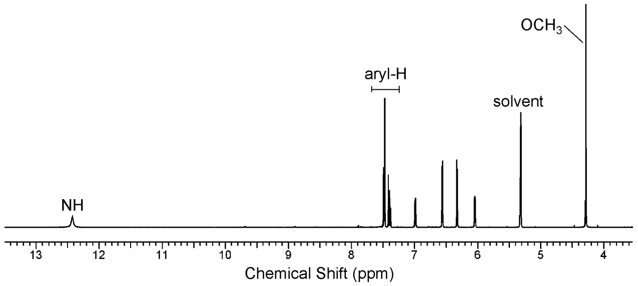


Fig. 6 ^{1}H NMR spectra of **5** in CD_2Cl_2.

and result in the NH peaks being highly downfield-shifted (12.94 ppm, Fig. 6).

Compounds **3**, **4** and **5** are unique and their formation is facile. The considerable electron deficiency of **3** results in the stabilization of carbanion intermediates (Scheme 2, before protonation) which allows for their formation. The chemical properties of dicyano-substituted vinyl dipyrromethene compounds render them good candidates as useful metal-chelating ligands due to the extended conjugation and near-planarity. Further research to address the continual challenge of yield improvement is underway.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

Notes and references

‡ Selected data for **3**: 8% yield (a small amount of compound **3** was lost during the isolation due to its poor solubility), λ_{max} (CH_2Cl_2, log ε)/nm 500 (4.64); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 11.18 (bs, 2H, NH), 7.64 (m, 2H, *A*H), 7.52-7.40 (m, 6H, aryl-H), 6.79 (d, *J* = 4.3, 2H, β-CH of inner pyrrole), 6.73 (d, *J* = 4.3, 2H, β-CH of inner pyrrole), 6.42 (m, 4H, β-CH of terminal pyrrole);^{13}C NMR (100 MHz, CD_2Cl_2) δ = 176.67, 156.04, 146.84, 142.83, 141.78, 136.71 (βC), 135.96, 135.66, 134.93 (αC), 134.19, 131.56 (*para*-C), 131.50, 128.82 (*meta*-C), 128.68 (*meta*-C), 126.19 (βC), 121.95 (βC), 114.57 (βC), 114.27, 30.28 (sp^{3}C); *m/z* HRESIMS found 802.9671, calcd. 802.9691 for $C_{38}H_{19}N_6O_2{}^{35}Cl_5{}^{37}Cl$ ($[M + H]^+$). Selected data for **4**: 80% yield, λ_{max} (CH_2Cl_2, log ε)/nm 335 (4.18), 492 (3.59), 680 (4.31), 735 (4.50).^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.94 (bs, 2H, NH),

7.59 (m, 2H, *A*-CH), 7.54–7.42 (m, 6H, aryl-H), 7.16 (d, J = 4.5, 2H, β-CH of inner pyrrole), 6.72 (d, J = 4.3, 2H, *β*-CH of inner pyrrole), 6.47 (dd, J = 4.1 and 1.2, 2H, β-CH of terminal pyrrole), 6.42 (dd, J = 4.3 and 2.2, 2H, β-CH of terminal pyrrole); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 140.04, 136.82 (αC), 135.95, 134.58, 133.75, 133.57 (βC), 131.47, 128.77 (aryl-C), 126.19 (βC), 125.77 (βC), 119.57, 115.38 (βC), 114.09; *m/z* HREIMS found 650.03271 (100%), calcd. 650.03471 for $C_{34}H_{18}N_6{}^{35}Cl_4$ (M^+). Selected data for **5**: 30% yield, λ_{max} (CH_2Cl_2, log ε)/nm 332 (4.51), 420 (3.94), 542 (4.48), 735 (4.50); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 12.43 (bs, 2H, NH), 7.54–7.35 (m, 6H, aryl-H), 6.99 (dd, J = 4.0 and 2.4, 2H, β-CH), 6.56 (d, J = 4.8, 2H, β-CH), 6.33 (d, J = 4.8, 2H, β-CH), 6.05 (dd, J = 4.4 and 1.6, 2H, β-CH), 4.29 (s, 6H, OCH_3); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 178.39, 160.22, 149.84, 144.99, 140.59, 138.79, 137.14 (βC), 136.90, 134.20, 131.24 (aryl-C), 129.45, 128.79 (aryl-C), 124.18, 122.67 (βC), 122.00, 120.70 (βC), 118.04 (βC), 113.99, 91.93, 58.36; *m/z* HRESIMS found 505.9636 (100%), calcd. 505.9633 for $C_{22}H_{12}N_3{}^{35}Cl_4O_3$ [$(M + H)^+$].

§ Crystal data for **3**: $C_{38}H_{18}N_6O_2Cl_6\cdot CH_2Cl_2$, T = 173 K, M = 888.21, triclinic, $P\bar{1}$ (no. 2), a = 11.2796(18) Å, b = 12.066(2) Å, c = 14.734(2) Å, α = 83.100(8)°, β = 79.807(8)°, γ = 89.782(8)°, V = 1959.0(6) Å^3, D_c = 1.506 g cm^{-3}, Z = 2, $R1$ = 0.053 [$I > 2.00\sigma(I)$], $wR2$ = 0.174 (all data), GOF = 1.17, CCDC 708612. Crystal data for **4**: $C_{34}H_{18}N_6Cl_4$, T = 173 K, M = 652.34, monoclinic, $P2_1/c$ (no. 14), a = 14.1530(16) Å, b = 10.3574(11) Å, c = 20.116(2) Å, α = 90.0°, β = 92.535(5)°, γ = 90.0°, V = 2945.8(6) Å^3, D_c = 1.471 g cm^{-3}, Z = 4, $R1$ = 0.033 [$I > 2.00\sigma(I)$], $wR2$ = 0.082 (all data), GOF = 1.02, CCDC 710025. Crystal data of **5**: $C_{22}H_{11}N_3Cl_2O_3$, T = 173 K, M = 507.14, triclinic, $P\bar{1}$ (no. 2), a = 7.8137(8) Å, b = 9.9057(11) Å, c = 14.0837(16) Å, α = 84.895(5)°, β = 77.368(5)°, γ = 81.828(5)°, V = 1051.0(2) Å^3, D_c = 1.603 g cm^{-3}, Z = 2, $R1$ = 0.030 [$I > 2.00\sigma(I)$], $wR2$ = 0.079 (all data), GOF = 1.03, CCDC 716868.

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